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(54) Title: METHOD FOR HYDROGEL SURFACE TREATMENT AND ARTICLE FORMED THEREFROM

(57) Abstract

A method of modifying the surface characteristics of a polymeric hydrogel, and a polymer article formed therefrom, without causing substantial swelling or distortion of the hydrogel. A preferred method includes photoinitiating of the surface of the article with a benzophenone and grafting a macromer having a number-average molecular weight greater than 1000 in the presence of UV irradiation. The preferred article is a siloxane-containing hydrogel, especially a soft contact lens.

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Method for Hydrogel Surface Treatment and Article Formed Therefrom

This invention relates broadly to surface modification of polymeric hydrogels. More particularly, the invention relates to the treatment of ophthalmic lenses, especially siloxane-containing hydrogel contact lenses.

Generally speaking, methods of treating polymer surfaces include (1) corona discharge, (2) surface degradation or oxidation by oxidizing agents such as chromic acid, (3) plasma treatment and/or plasma polymerization, (4) graft polymerization, and (5) coating.

US 4,892,402, for example, discloses a method for making hard contact lenses more hydrophilic. The method involves contacting a hard lens with a treatment solution containing a hydrophilic monomer, at least one photosensitizer selected from aromatic ketones or quinones, and a solvent, and then irradiating the lens with ultraviolet light. Thus, the disclosed method is a solvent-based polymerization. Benzophenone is an example of a suitable photosensitizer.

While there exist numerous methods of surface treating polymeric articles, there remain problems with the surface treatment of hydrogel materials, especially those suited as ophthalmic lenses. One problem with many surface grafting techniques is that monomer in the treatment solution may penetrate the hydrogel's polymer matrix, and subsequently bind to the polymer below the article's surface. If substantial monomer penetration occurs, the treated polymeric article may swell and distort from the original shape. Even slight distortion can produce substantial optical distortions in an ophthalmic lens. Thus, there remains a need for a method of surface treating hydrogel materials without substantially modifying the shape of the hydrogel.

An object of the invention is to modify the surface properties of a polymeric hydrogel, without substantially modifying the shape of the hydrogel.

A further object of the invention is to increase the hydrophilicity of the surface of a polymeric hydrogel, without substantially modifying the shape of the hydrogel.

Another object of the invention is to increase the hydrophilicity of the surface of a hydrophilic ophthalmic lens, without substantially impairing the optical properties of the lens.

The present invention relates to a method of treating the surface of a polymeric article, which includes the following steps:

(a) immersing a polymeric article in a first solution including a benzophenone and at least one solvent for a predetermined time period;

(b) removing said article from said first solution;

(c) evaporating at least a portion of said solvent from said article;

(d) placing said article in a second solution containing at least one macromer; and

(e) applying radiation to said article for a period sufficient to cause at least a portion of said macromers to bond to the surface of said article,

wherein said macromer has a size sufficiently large such that no substantial amount of macromer penetrates said article and causes substantial distortion of said article.

Another embodiment is a polymeric hydrogel article including a core bulk material and a surface coating. The surface coating is formed by graft polymerization with surface photoinitiation in the presence of a benzophenone. The grafted groups are formed from one or more macromers having a size sufficiently large such that no substantial amount of macromer penetrates said lens causing substantial distortion of said lens. The preferred polymeric article is a soft contact lens including a bulk material which is a silicone-containing hydrogel.

The following terms are defined at the outset in order to facilitate a clear understanding of the present invention. Certain terms are defined subsequently in the text because of the limited use herein.

The term "copolymer", as used herein, means polymers formed from two or more monomers or macromers. Thus, copolymer includes terpolymers and the like.
The term "macromer" as used herein refers to a species having at least one unsaturated bond and having at least two repeating monomer units.

The term "hydrogel", as used herein, refers to a polymeric material which contains at least about 10 weight percent water when fully saturated.

The present invention is related to a method of modifying the surface characteristics of a polymeric article, e.g. a polymeric hydrogel. The preferred polymeric articles useful in accordance with the present invention are silicone-containing hydrogel materials. A more preferred subclass of articles which may be treated in accordance with the present invention are ophthalmic lenses, including without limitation thereto, contact lenses, intraocular lenses (i.e., implants), and lenses designed for delivery of pharmaceuticals or other agents to the ocular environment. Contact lenses are the most preferred treatment article, in particular soft contact lenses.

The term "Photosensitizer", as used herein include, without limitation thereto, benzophenone, thioxanethen-9-one , 2-acetonaphthone, mixtures thereof and the like.

The term "benzophenone", as used herein, means benzophenone and derivatives thereof which are suited to initiating surface bonding to a contact lens polymer in the presence of applied light, i.e., derivatives suited to photoinitation of surface polymerization. Thus, "benzophenone" includes, without limitation thereto, 2-amino benzophenone; 2-amino-5-chloro benzophenone; 2-amino-4'-methyl benzophenone; 2-amino-5-methyl benzophenone; 2-amino-5-nitro benzophenone; 3-amino benzophenone; 3-amino-4-methyl benzophenone; 3-amino-4'-methyl benzophenone; 4-amino benzophenone; 4-amino-3-methyl benzophenone; 4-amino-4'-methyl benzophenone. A more preferred group of benzophenones includes benzophenone; 4-fluorobenzophenone; 4-chlorobenzophenone; 4-benzoylbenzoic acid; 3,3'-4,4'-benzophenone tetracarboxylic dianhydride, Mischler's ketone, and mixtures thereof.

The first treatment solution is intended to functionalize the lens surface, i.e., to prepare the surface for facile grafting or bonding of macromeric species thereto. The solution may include about 0.1 to 10 millimoles/liter (mmol/L) benzophenone, about 10 to 50 weight percent solvent, and about 90 to 50 weight percent water, in which the water and solvent weight percentages are based on the water/solvent mixture. More preferably, the first solution includes about 0.5 to 5 weight percent benzophenone, about 20 to 40 weight percent solvent, and about 60 to 40 weight percent water. Suitable solvents for benzophenone include, without limitation thereto, short chain alcohols such as isopropanol, ethanol, and the like. Preferably, the solvent is miscible with water, so that a homogeneous system is produced.

While the invention is not limited to theoretical explanations of operability, the following theory is offered to better enable the reader to understand the invention. It is believed that the benzophenone separates out of the solution at unduly low solvent levels. Thus, low solvent levels may create a heterogeneous system, and promote non-uniform surface functionalization. However, increasing solvent concentration may cause the lens to swell. The swelling is believed to increase the lens porosity. At excessively high solvent concentrations, the pores in the lens material are large enough to allow penetration of the macromer into the lens structure, thereby causing lens deformation and optical distortions. Thus, a proper surface treatment is achieved by maintaining the solvent concentration high enough to provide a homogenous mixture (and uniform treatment), while maintaining the solvent concentration below the point at which unacceptable macromer penetration (and optical distortion) occurs.

The first solution may be exposed to the lens for a period of about 1 to 30 minutes, more preferably about 5 to 20 minutes, and most preferably about 8 to 12 minutes. Subsequent to contact with the first solution, the lens is removed from the first solution and evaporated under conditions which do not substantially damage the lens.

Evaporation of the solvent is preferred. Evaporation may be accomplished in a number of ways, including air drying and application of a limited amount of heat or air currents. The lens may be air dried for about 30 minutes to 3 hours, more preferably about 1 to 2 hours, depending on the temperature and relative humidity. Subsequent to air drying, the lenses may be placed in a nitrogen atmosphere. Then, a vacuum may be generated, preferably at a pressure of less than about 0.5 millibars. More preferably, the lenses are nitrogen and vacuum treated during two or more cycles.

The amount of water and/or solvent remaining in the lens depends on the specific treatment composition selected and the core polymer material chosen for treatment. It is preferable to remove the bulk of the solvent so that the photosensitizer remains on the surface of the article to be treated. Preferably, the solvent and water are substantially completely evaporated, i.e., less than 50 weight percent solvent/water remains in the lens. More preferably, less than about 25 weight percent solvent/water remains in the lens.

Preferably subsequent to the evaporation step, the lens is contacted with a second solution including macromer. The second solution preferably includes about 1 to 50 weight percent macromer and about 99 to 50 weight percent water. More preferably, the second solution includes about 5 to 10 weight percent macromer and about 95 to 90 weight percent water.

After contacting the lens with the macromer-containing solution, grafting of the macromer to the lens surface is initiated by applying ultraviolet light in an amount and for a time sufficient to cause a substantial amount of the macromer to bond to the lens surface. The UV light may be applied at an intensity of about 25 to about 100 milliwatts per square centimeter (mW/cm^2) for a period of about one minute to one hour. More preferably, the UV light is applied at an intensity of about 50 to about 60 mW/cm^2 for a period of about 5 to 20 minutes.

Subsequent to photoinitiation of the macromer-bonding reaction, the lens may be subjected to an optional step of extraction to remove any undesirable remaining solvent. For example, the lens may be rinsed with a solution of deionized water, followed by a solution of about 10 to 30 weight percent isopropanol with about 90 to 70 weight percent water.

A wide variety of hydrophilic macromers are useful in the present invention, including without limitation thereto, polalkylene oxides such as polyethylene oxide; polydimethylacrylamides; polyvinyl alcohols; poly(acrylates); poly(methacrylates) such as poly(2-hydroxyethyl methacrylate); poly(N-vinylpyrrolidone); poly(acrylamides) such as poly(N,N-dimethylacrylamide); derivatives, copolymers, mixtures thereof, and the like. A more preferred group of hydrophilic macromers includes polyethylene oxides, polyvinyl alcohols, and polyacrylamides, especially poly(N,N-dimethylacrylamide). Furthermore, it may be possible to apply a mixture of functionalized macromers with polymers.

However, the macromers useful in accordance with the present invention must have a size sufficient to prevent the macromer from substantially penetrating the polymer network of the lens. If the polymer network is penetrated, the lens may swell and become distorted. Minor amounts of swelling can cause intolerable amounts of deviation in the intended overall or localized optical power of the lens, thereby distorting the vision of the ultimate consumer. Also, a poor fit to the consumer's eye can occur if the lens swells. Moreover, the unpredictability of the swelling can further complicate matters. Accordingly, the macromers useful in the present invention have a size sufficiently large such that no substantial amount of macromer penetrates the article to be treated (e.g., a contact lens) causing substantial distortion of the article.

With respect to optical lenses, the macromers preferably have a size sufficiently large to produce a contact lens having a final diameter which differs less than 10% with respect to the diameter of the untreated lens. More preferably, the lens diameter changes less than about 5%, even more preferably, less than about 2%.

One method of measuring the relative size of a macromer is molecular weight. The preferred molecular weight of the macromers is a number-average molecular weight greater than about 500. A more preferred number-average molecular weight is above about 1000.

The previous disclosure will enable one having ordinary skill in the art to practice the invention. Reference to the following examples is suggested.

EXAMPLE I

Hydrogel contact lenses are soaked in a first solution including about 3 mmol/L benzophenone in a 70/30 weight ratio water/isopropyl alcohol mixture. The lenses are air dried at room temperature for about 90 minutes. The lenses are placed in a nitrogen atmosphere in a chamber which is evacuated under 2 cycles vacuum in order to degas the lenses.

After degassing, the lenses are placed into molds containing a solution of polyvinylalcohol (PVA) macromer at a concentration of about 5 weight percent in water. The macromer has a number-average molecular weight of about 16,000 grams/mol.

The molds, which contain the lenses and macromer solution, are subjected to ultraviolet light at an intensity of about 5.8 to 6.0 mW/cm^2 for about 10 minutes, in order to bond the macromer to the lens surface.

After treatment, the lenses are removed from the molds and rinsed with deionized water, followed by a rinsing with a 20/80 volume ratio isopropanol/water solution. The lenses are autoclaved at a temperature of about 121°C for a period of about 30 minutes before measurements are taken.

COMPARATIVE EXAMPLE II

The treatment procedures described in Example I are followed substantially in this Example, with the exception being that the macromer is a polyoxyethylene having number-average molecular weight of about 1000.

CLAIMS

1. A method of treating the surface of a polymeric article, comprising the steps of:
(a) immersing a polymeric article in a first solution including a photosensitizer and at least one solvent for a predetermined time period;
(b) removing said article from said first solution;
(c) evaporating at least a portion of said solvent from said article;
(d) placing said article in a second solution containing at least one macromer; and
(e) applying radiation to said article for a period sufficient to cause at least a portion of said monomers or macromers to bond to the surface of said article,
wherein said macromer has a size sufficiently large such that no substantial amount of macromer penetrates said article causing substantial distortion of said article.

2. A method of claim 1, wherein said photosensitizer is selected from the group consisting of benzophenone, thioxanethen-9-one , 2-acetonaphthone, mixtures thereof and the like.

3. A method of claim 2, wherein said photosensitizer is a benzophenone.

4. A method of claim 3, wherein said benzophenone is selected from the group consisting of benzophenone; 4-fluorobenzophenone; 4-chlorobenzophenone; 4-benzoylbenzoic acid; 3,3'-4,4'-benzophenone tetracarboxylic dianhydride, Mischler's ketone, and mixtures thereof.

5. A method of claim 1, wherein said macromer has a number-average molecular weight of at least 500.

6. A method of claim 4, wherein said macromer has a number-average molecular weight of at least 1000.

7. A method of claim 1, wherein said article is a hydrogel, having at least about 10 weight percent water when fully hydrated.

8. A method of claim 1, wherein said macromer is selected from the group consisting of polyalkylene oxides, polydimethyl acrylamides, mixtures thereof, and copolymers thereof.

9. A method of claim 10, wherein said macromer is a polyethylene oxide.

10. A method as recited in claim 1, wherein said macromer is a polyalkylene oxide having a number-average molecular weight greater than about 1000.

11. A method of claim 1, wherein said polymeric article is formed from a silicon-containing polymer.

12. A method of claim 18, wherein said silicon-containing polymer is a polydimethylsiloxane.

13. A method of claim 1, wherein said article is a contact lens.

14. A polymeric article having a surface with properties different from the bulk polymeric article material, said polymeric article comprising:

(a) a polymeric article bulk material selected from the group consisting of siloxane-containing polymers;

(b) a surface coating on said polymeric article bulk material, said surface coating including pendant groups formed by graft polymerization by surface photoinitiation with a benzophenone, said pendant groups being formed from one or more macromers having a size sufficiently large such that no substantial amount of macromer penetrates said lens causing substantial distortion of said article.

15. An article of claim 21, wherein said article is selected from the group consisting of contact lenses, intraocular lenses, implants, and ophthalmic agent delivery devices.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 G02B1/04 C08J7/18

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 G02B C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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